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(54) **Process of protection of dyes on textiles to the attack of bleaching agents such as hydrogen peroxide, perborates and percarbonates**

(57) The invention refers to a process of colour protection of dyed textile goods to the attack by peroxides, either due to industrial bleaching or peroxide application in the washing machine, such as occurs when the textiles are prebleached or washed with detergents that contain peroxides such as perborates and percarbonates. The most sensitive dyes are reactive and sulphur dyes for cotton. Some dyes belonging to these classes lose colour strength and alter their hue.

In this invention a new process of colour protection for dyed goods is revealed, by the application of quenchers, which when applied simultaneously with the peroxide, inhibit the peroxide attack on the dyes present in the textile fibres.

The products claimed in this invention to work as efficient quenchers and colour protectors are ascorbic acid, DABCO or 1,4-diaza-2,2,2-bicyclooctane and diphenylamine.

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## Description

[0001] Textile cotton and synthetic goods when washed by the consumer are usually washed with detergents containing peroxides, namely perborates and percarbonates. Both these products liberate hydrogen peroxide when in an alkaline medium. The objective is to bleach the fibres every time the clothes are washed, and also to disinfect the textile goods, since the peroxides have an anti-bactericide action.

[0002] The problem is that peroxides also attack some more sensitive synthetic dyes, such as sulphur dyes and some reactive and direct dyes, deteriorating the colour, with loss of colour strength and alteration of hue. Some chromophores which otherwise are not sensitive, in the presence of heavy metal ions, such as  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$ , deteriorate in the same way as the sensitive chromophores. An example of these are found in whole classes of dyes, otherwise not sensitive, such as disperse dyes for synthetic fibres.

[0003] Usually the attack of peroxides on dyes is through the excited species of singlet oxygen, or through free radicals formed by the decomposition of the peroxide.

[0004] Some products, known as quenchers, are effective in inhibiting the attack of oxygen, in its excited singlet or triplet state, or inhibiting the attack of free radicals.

[0005] The process we claim is through the application of singlet oxygen quenchers, such as DABCO, 1,4-diaza-2,2,2-bicyclooctane, or quenchers of free radicals, such as ascorbic acid and diphenylamine. These products are water-soluble and can be applied mixed with other aqueous products, such as liquid detergents. To be applied with a solid detergent they should be first microencapsulated, since they are either unstable in the presence of oxidants, such as ascorbic acid, or volatile and skin irritant, such as DABCO and diphenylamine. The microcapsule should then release the quencher when the conditions for application are met, immersed in water, rise in temperature or pH. Examples of these polymers are polyvinylpyrrolidone and polyethylene glycol, which are water soluble or urea-formaldehyde type polymers, which are destroyed in alkaline conditions.

[0006] The attack of peroxides on dyes by perborate, percarbonate or hydrogen peroxide, should only occur above  $60^\circ\text{C}$ , but in the presence of peroxide activators, such as T.A.E.D., tetraacetylene diamine, it occurs at lower temperatures, down to  $40^\circ\text{C}$  or even lower temperatures. The quenchers mentioned also function at these temperatures in the presence of T.A.E.D.

[0007] To evaluate the fastness of the colours to washing with detergents the standard test ISO C06-A2, B2 and C2, which consists in treating the textile sample, together with a blank, with a solution of 4 g/l of standard detergent ECE, 1 g/l of sodium perborate, at  $60^\circ\text{C}$  for 30 minutes. Under these conditions we notice some alteration in colour of the most sensitive dyes and some

staining of the blank with the dyes with the most affinity. For evaluation the grey scale can be used, with a classification of 1-5, with the best result at 5 and the worse at 1. If we use the referred quenchers, in solution or microencapsulated, we verify that the colour alteration and the staining are less, usually 1 point higher, which can mean the difference between a pass and a fail. In a practical situation commercial detergents are used and these contain between 15 and 30% of sodium perborate. The number of washes during the life of the textile goods are usually more than one, and as the effect of peroxides is cumulative, colour degradation becomes much more pronounced in subsequent washes to the first wash. The standard test ISO 105 C06-A2, B2, C2, doesn't reflect this situation.

[0008] Another similar situation to bleaching during domestic washing, is that in which peroxides are applied to textile cotton fabrics or knitwear already dyed, with the purpose of saving energy, water or time. In the case of cotton woven fabric the reason for bleaching after dyeing might be to weave yarn in the grey state, before bleaching, since it will have less breakages during the weaving process. In the case of cotton knitwear with reactive dyes, bleaching before dyeing is followed by rinsing, which are water, time and energy consuming processes. Bleaching after dyeing, or post-bleaching, does not need these rinsing stages. The problem in these processes is that if the dyes present in the goods are sensitive to peroxides, such as reactive and sulphur dyes, they would deteriorate and would make these processes not viable.

[0009] If the quenchers already referred are applied simultaneously with the peroxide, the dyes are protected and the post-bleaching can be applied safely.

### Example 1

[0010] Sample of 4g of cotton fabric dyed with the dye C.I. Reactive Orange 64, subjected to a washfastness test, in an aqueous solution of 4 g/l of detergent ECE, 1 to 5 g/l of sodium perborate, 1 g/l of sodium carbonate, for 30 minutes at  $60^\circ\text{C}$ , to which is added 0,1 to 5% of 1,4-diaza-222-bicyclooctane. The colour of the textile sample doesn't alter under these conditions

### Example 2

[0011] A sample of 4g of cotton fabric dyed with the dye C.I. Disperse Blue 56, subjected to a washfastness test, in an aqueous solution of 4 g/l of detergent ECE, 1 to 5 g/l of sodium perborate, 1 g/l of sodium carbonate, for 30 minutes at  $60^\circ\text{C}$ , and 0,5 to 10 g/l of copper sulphate, to which is added 0,1 to 5% of 1,4-diaza-222-bicyclooctane. The colour of the textile sample doesn't alter under these conditions.

## Example 3

[0012] A sample of 4g of cotton fabric dyed with the dye C.I. Reactive Blue 204, subjected to a washfastness test, in an aqueous solution of 4 g/l of detergent ECE, 1 to 5 g/l of sodium perborate, 1 g/l of sodium carbonate, for 30 minutes at 60°C, to which is added 0,1 to 5% of 1,4-diaza-222-bicyclooctane. The colour of the textile sample doesn't alter under these conditions.

## Example 4

[0013] A sample of 4g of cotton fabric dyed with the dye C.I. Solubilised Sulphur Black 1, subjected to a washfastness test, in an aqueous solution of 4 g/l of detergent ECE, 1 to 5 g/l of sodium perborate, 1 g/l of sodium carbonate, for 30 minutes at 60°C, to which is added 0,1 to 5% of ascorbic acid. The colour of the textile sample doesn't alter under these conditions

## Example 5

[0014] A sample of 4g of cotton fabric dyed with dye C.I. Reactive Orange 64, subjected to a washfastness test, in an aqueous solution of 4 g/l of detergent ECE, 1 to 5 g/l of sodium perborate, 1 g/l of sodium carbonate, for 30 minutes at 60°C, to which is added 0,1 to 5% of ascorbic acid. The colour of the textile sample doesn't alter under these conditions

## Example 6

[0015] A sample of 4g of cotton fabric dyed with the dye C.I. Reactive Orange 64, subjected to a washfastness test, in an aqueous solution of 4 g/l of detergent ECE, 1 to 5 g/l of sodium perborate, 1 g/l of sodium carbonate, for 30 minutes at 60°C, to which is added 0,1 to 5% of diphenylamine. The colour of the textile sample doesn't alter under these conditions

## Example 7

[0016] A sample of 4g of cotton fabric dyed with the dye C.I. Reactive Orange 64, subjected to a washfastness test, in an aqueous solution of 4 g/l of detergent ECE, 1 to 5 g/l of sodium perborate, 1 g/l of sodium carbonate, for 30 minutes at 60°C, to which is added 0,1 to 5% of 1,4-diaza-2,2,2-diazabicyclooctano microencapsulated with a melamine-formaldehyde polymer. The colour of the textile sample doesn't alter under these conditions

## Example 8

[0017] A sample of cotton fabric, having a design with unbleached and colour yarns, dyed with reactive or sulphur dyes, bleached with hydrogen peroxide, in an alkaline medium, and simultaneously with 0,1 to 5 g/l of

ascorbic acid. The colour of the dyed yarns doesn't change under these conditions.

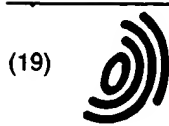
## Example 9

[0018] A sample of knitwear dyed with reactive dyes, bleached with hydrogen peroxide, in an alkaline medium, and simultaneously with 0,1 to 5 g/l of ascorbic acid. The colour of the dyed knitwear doesn't change under these conditions.

## Claims

1. Process of treating dyed textile goods, consisting of the application of the product ascorbic acid, for the protection of the dyes present in the textile goods to the attack of peroxides during industrial bleaching with hydrogen peroxide, or its application in domestic washing machines simultaneously with perborates or percarbonates.
2. Process according to claim n° 1, but applying instead the product 1,4-diaza-2,2,2-bicyclooctane, DABCO, for the protection of dyes to peroxides.
3. Process according to claim n° 1, but applying the product diphenylamine for the protection of dyes to peroxides.
4. Process according to claim n° 1, but applying the products referred in claims 1-3, microencapsulated with a polymer, which breaks down when added to the bleaching solution, freeing in so doing the active product.
5. Process according to claim n° 4, in which the polymer is specifically polyvinylpyrrolidone, PVP.
6. Process according to claim n° 4, in which the polymer is specifically a polymer based on derivatives of urea and formaldehyde monomers.
7. Process according to claim n° 4, in which the polymer is specifically polyethyleneglycol.
8. Process according to claim n° 4, in which the polymer is specifically poly-hydroxyethyl-methacrylate, Poly (HEMA)
9. Process according to any of the previous claims, in which the application of the peroxides is done simultaneous with detergent in a washing machine.
10. Process according to claim n° 9, in which the detergent also contains peroxide activators, such as T. A.E.D., tetraacetylenethylenediamine.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 12 1860

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Place of search		Date of completion of the search	Examiner
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<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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